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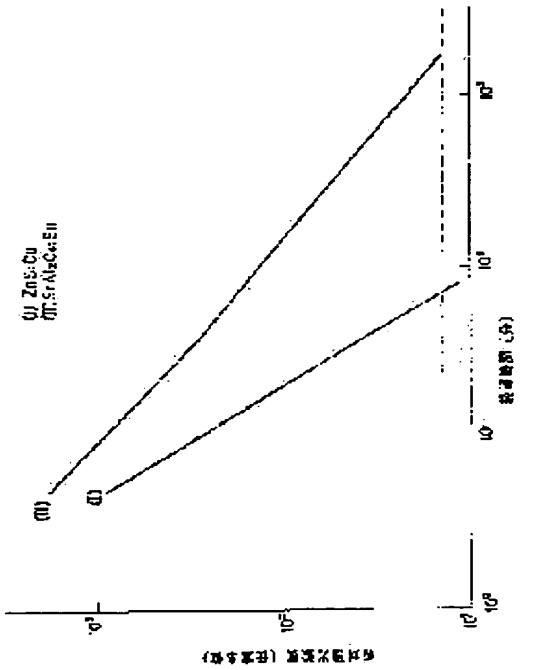
(54) LUMINOUS FLUORESCENT SUBSTANCE

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a luminous fluorescent substance having a long-time afterglow characteristic and also being chemically stable, and excellent in long-term lightfastness.
SOLUTION: This luminous fluorescent substance features comprising a compound represented by the formula: MAl2O4 (wherein M is at least one of metallic elements selected from the group consisting of calcium, strontium and barium) in a state of host crystal, and being mixed with europium as an activator in an amount of 0.001-10 mol% based on the quantity of a metallic element represented by M and with at least one of elements selected from the group consisting of manganese, tin and bismuth as a coactivator in an amount of 0.001-10 mol% based on the quantity of a metallic element represented by M.



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* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] MAl 2O4 With the compound expressed, M The compound which consists of at least one or more metallic elements chosen from the group which consists of calcium, strontium, and barium is made a mother crystal. It adds 10% or less more than 0.001 % by mol % to the metallic element which expresses a europium with M to this as an activator. Furthermore, phosphorescent materials characterized by adding at least one or more elements of a group which consist of manganese, tin, and bismuths as a coactivator 10% or less more than 0.001 % by mol % to the metallic element expressed with M.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the new phosphorescent materials which have the decay characteristic of long duration extremely while it is excellent in lightfastness mainly available as an object for the Nighttime display out of phosphorescent materials, especially indoor.
[0002]
[Description of the Prior Art] Promptly, if the afterglow time amount of a fluorescent substance is very short and an external stimulus is generally stopped, although decreased, even after stimulating the luminescence by ultraviolet rays etc. rarely and it stops the stimulus, it has some in which afterglow is accepted over remarkable long duration (several 10 minutes - several hours) with the naked eye, and is calling these phosphorescent materials or a phosphor in distinction from the usual fluorescent substance.
[0003] As these phosphorescent materials, although sulfide fluorescent substances, such as CaS:Bi (purple/blue color luminescence), CaSrS:Bi (blue luminescence), ZnS:Cu (green luminescence), and ZnCdS:Cu (yellow - orange luminescence), are known, there are many troubles in respect of [— any of these sulfide fluorescent substances are chemically unstable, or inferior to lightfastness —] practical use. If especially moisture existed, in order that might photodissociate by ultraviolet rays, and it might be discolored in black or the zinc sulfide system phosphorescent materials (ZnS:Cu) used chiefly in a current commercial scene might also carry out a brightness fall, use for an application which is put outdoors to direct daylight is difficult, and the applications, such as a watch with a luminous dial and the refuge leading sign and indoor Nighttime display, were limited.
[0004] Moreover, even if it was the case where this zinc sulfide system fluorescent substance was used for a watch with a luminous dial, the afterglow time amount which can recognize that time of day with the naked eye was about 2 hours from about 30 minutes, and the present condition was using the luminous paint of the self-luminescence which adds the radioactive substance to a fluorescent substance, stimulates with that energy practical, and always emits light.
[0005]
[Problem(s) to be Solved by the Invention] Then, in view of the present condition like the above-mentioned, this invention person has the decay characteristic of long duration far compared with a commercial sulfide system fluorescent substance, and it is still more chemically stable and he used to aim at offer of the phosphorescent materials which are excellent in lightfastness over a long period of time.
[0006]
[Means for Solving the Problem] Its attention is paid to the aluminate of the alkaline earth metal which carried out activation of the europium etc. as a completely different new phosphorescent-materials ingredient from the sulfide system fluorescent substance known from the former. As a result of conducting various experiments, this phosphorescent-materials ingredient has the decay characteristic of long duration far compared with a commercial sulfide system fluorescent

substance. Even if it is chemically stable from being an oxide system, and it can check excelling in lightfastness, the conventional trouble can be solved entirely and it does not contain activity, furthermore, as the luminous paint in which a check by looking during 1 evening is possible, or a pigment It becomes clear that it becomes possible to offer the phosphorescent materials of long afterglow applicable to various applications.
[0007] As phosphorescent materials which were mentioned above, a thing according to claim 1 MAl 2O4 With the compound expressed, M The compound which consists of at least one or more metallic elements chosen from the group which consists of calcium, strontium, and barium is made a mother crystal. It adds 10% or less more than 0.001 % by mol % to the metallic element which expresses a europium with M to this as an activator. Furthermore, it is characterized by adding at least one or more elements of a group which consist of manganese, tin, and bismuths as a coactivator 10% or less more than 0.001 % by mol % to the metallic element expressed with M.
[0008] Moreover, composition of these phosphorescent materials is faced and it is boric acid as flux. It can add in 1 - 10% of the weight of the range. The flux effectiveness is lost here as an addition is 1 or less % of the weight, if 10 % of the weight is exceeded, it will solidify, and subsequent grinding and classification become difficult.
[0009]
[Example] The following and MAl 2O4 Sequential explanation of the example of this invention expressed is given about the case where various the classes and concentration of the concentration of the class of metallic element (M) and the europium as an activator or a coactivator are changed. Although strontium is first used as a metallic element (M) and a europium is used as an activator, the phosphorescent materials when not using a coactivator are explained as an example 1.
Example 1.SrAl 2O4 : To strontium-carbonate 146.1 g (0.99 mols) and alumina 102 g (one mol) of the composition and the property sample 1-(1) special grade chemical of Eu fluorescent substance, as an activator It is europium oxide (Eu 2O3) about a europium. 1.76g (0.005 mol) addition is carried out. Furthermore, it is boric acid as flux. After carrying out 5g (0.08 mols) addition and fully mixing using a ball mill, 1300 degrees C of this sample were calcinated for 1 hour using the electric furnace in the nitrogen-hydrogen mixed-gas (97:3) air current (flow rate: 0.1 liter per minute). It is what cooled over about 1 hour to the room temperature after that, classified the obtained compound fine particles with the screen, and passed 100 meshes Fluorescent substance sample 1-(1) It carried out.
[0010] The result of having analyzed the crystal structure of the compounded fluorescent substance by XRD (X diffraction) was shown in drawing 1 . The fluorescent substance obtained from the property of a diffraction peak is SrAl 2O4. Having Spinel structure became whether to be **. The excitation spectrum of this fluorescent substance and the emission spectrum of the afterglow after a stimulus halt were shown in drawing 2 .
[0011] It became clear from drawing that it is green luminescence whose peak wavelength of an emission spectrum is about 520nm. Next, this SrAl 2O4 : The result of having measured the decay characteristic of Eu fluorescent substance with the commercial item as compared with the decay characteristic of the ZnS:Cu phosphorescent materials (Nemoto [& Co., Ltd.] make: a name of article GSS, emission-peak-wavelength:530nm) which emit light green was shown in drawing 3 and Table 2.
[0012] Measurement of the decay characteristic is 200 by the Dafter keeping 0.05g of fluorescent substance powder to planchet made from aluminum with a bore of 8mm **** picking (sample thickness: 0.1 g/cm2) and about 15-hour in the dark and eliminating afterglow 65 standard light source. It stimulates for 10 minutes with the brightness of looks, and subsequent afterglow is measured with the brightness measuring device using the photomultiplier tube. SrAl 2O4 according to this invention so that clearly from drawing 3 : The attenuation of the afterglow of Eu fluorescent substance is also very greatly loose, and it turns out that an afterglow difference on the strength with ZnS:Cu phosphorescent materials becomes large with elapsed time. Moreover, although the broken line showed the level (equivalent to the brightness of about 0.3 mCd/m2) of the luminescence reinforcement which can enough be recognized with the naked

eye all over drawing, it is this SrAl 2O4. : It is presumed [that that luminescence can be recognized also after / of the decay characteristic of Eu fluorescent substance / about 24 hours, and]. This SrAl 2O4 that actually passed after the stimulus for 15 hours : When Eu fluorescent substance was observed with the naked eye, that afterglow was fully able to be checked.
[0013] moreover, sample 1- in Table 2 — (1) **** — the relative value to the reinforcement of ZnS:Cu phosphorescent materials showed the afterglow reinforcement of after [a stimulus halt] 10 minutes, 30 minutes, and 100 minutes after. SrAl 2O4 by this invention from this table : The afterglow brightness of Eu fluorescent substance is 2.9 of ZnS:Cu phosphorescent materials after 10 minutes. It is twice and it turns out after 100 minutes that they are 17 times. SrAl 2O4 furthermore according to this invention : The result of having investigated the thermoluminescence property (glow curve) from the room temperature at the time of carrying out the luminous stimulus of the Eu fluorescent substance to 250 degrees C using the TLD reader (KYOKKO TLD-2000 system) was shown in drawing 4 . The thermoluminescence of drawing to this fluorescent substance consists of three glow peaks, about 40 degrees C, 90 degrees C, and 130 degrees C, and it turns out that about 130-degree C peak is the Maine glow peak. SrAl 2O4 according to this invention in the light of the Maine glow peak of the ZnS:Cu phosphorescent materials shown with the broken line in drawing being about 40 degrees C : The deep trapping level equivalent to the elevated temperature 50 degrees C or more of Eu fluorescent substance enlarges the time constant of afterglow, and is considered to have contributed to the light storage property covering long duration.
[0014] Sample 1-(2) - (7) SrAl 2O4 of a compounding ratio expressed in Table 1 to which the concentration of a europium was changed by the approach as the above-mentioned that next it is the same : Eu fluorescent substance sample (sample 1-(2) - (7)) was adjusted.
[0015]
[Table 1]

試料	原料配合比		
	炭酸ストロンチウム	アルミナ	ユウロピウム
試料1-(2)	0.99958 モル	1.0 モル	0.00001モル
(3)	0.9995	1.0	0.00005
(4)	0.995	1.0	0.0025
(5)	0.97	1.0	0.015
(6)	0.90	1.0	0.05
(7)	0.80	1.0	0.1

[0016] This sample 1-(2) - (7) It is the result of having investigated the decay characteristic 1-(1) With the result of having investigated the decay characteristic, it was shown all over Table 2. This table 2 shows excelling ZnS:Cu phosphorescent materials in the decay characteristic including the brightness of 10 minutes after as it is the range whose addition of Eu is 0.0025-0.05 mols. When the addition of Eu is merely 0.00001 mols, or even if it is the case where it is 0.1 mols, when 30 minutes or more pass after a stimulus halt also shows coming to have larger brightness than ZnS:Cu phosphorescent materials.
[0017] Moreover, since Eu is expensive, when the fall of economical efficiency and the decay characteristic by concentration quenching is taken into consideration, there will be no semantics in carrying out Eu more than 0.1 mol (ten-mol %) not much. On the contrary, since larger brightness than ZnS:Cu phosphorescent materials is obtained when 30 minutes or more pass after a stimulus halt although Eu is inferior to ZnS:Cu phosphorescent materials by after [10 minutes] brightness with brightness from 0.00001 (0.001-mol %) to 0.00005 mols (0.005-mol %), judging from the decay characteristic, the addition effectiveness of Eu used as an activator is clear.

[0018] Furthermore, SrAl 2O4 : From it being an oxide system, Eu fluorescent substance is chemically stable compared with the conventional sulfide system phosphorescent materials, and excellent in lightfastness (Table 24 and 25 reference).
[0019]
[Table 2]

試料	10分後輝度	30分後輝度	100分後輝度
ZnS:Cu Std.	1.00	1.30	1.00
試料1-(1)	2.90	6.61	17.0
(2)	0.41	1.20	3.10
(3)	0.58	1.50	4.80
(4)	2.40	4.50	13.5
(5)	3.01	7.04	19.2
(6)	1.10	2.70	10.3
(7)	0.32	1.11	3.02

[0020] Next, the phosphorescent materials at the time of using a dysprosium as a coactivator further are explained as an example 2, using a europium as an activator, using strontium as a metallic element (M).
Example 2.SrAl 2O4 : Eu, As an activator a europium by europium oxide (Eu 2O3) to strontium-carbonate 144.6 g (0.98 mols) and alumina 102 g (one mol) of the composition and the property sample 2-(1) special grade chemical of Dy fluorescent substance 1.76g (0.005 mols), Furthermore, 1.87g (0.005 mol) addition of the dysprosium is carried out with an oxidization dysprosium (Dy 2O3) as a coactivator. Furthermore, after doing 5 g (0.08 mols) addition of boric acid as flux and fully mixing using a ball mill, 1300 degrees C of this sample were calcinated for 1 hour using the electric furnace in the nitrogen-hydrogen mixed-gas (97:3) air current (flow rate: 0.1l. per minute). It is what cooled over about 1 hour to the room temperature after that, classified the obtained compound fine particles with the screen, and passed 100 meshes Fluorescent substance sample 2-(1) It carried out.
[0021] It is the result of having investigated the decay characteristic of this fluorescent substance by the same approach as the above-mentioned Sample 2-(1) of drawing 5 and Table 4 It was shown. SrAl 2O4 according to this invention so that clearly from drawing 5 : Especially, the brightness at the time of the early stages of afterglow is very high as compared with ZnS:Cu phosphorescent materials, and the fact are Eu, are [of Dy fluorescent substance / afterglow] brightness, and that the time constant of the attenuation is also large shows that they are epoch-making high brightness phosphorescent materials. The afterglow level on the strength which was shown all over drawing and which can be checked by looking, and this SrAl 2O4 : It is identifiable in that luminescence also after [of the decay characteristic of Eu and Dy fluorescent substance] about 16 hours.
[0022] SrAl 2O4 by this invention from a table although the afterglow reinforcement of after [a stimulus] 10 minutes, 30 minutes, and 100 minutes after is shown in Table 4 by the relative value to the reinforcement of ZnS:Cu phosphorescent materials : The afterglow brightness of Eu and Dy fluorescent substance is 12.5 times the ZnS:Cu phosphorescent materials after 10 minutes, and it turns out after 100 minutes that they are 37 times. SrAl 2O4 furthermore according to this invention : The result of having investigated the thermoluminescence property (glow curve) from the room temperature at the time of carrying out the luminous stimulus of Eu and the Dy fluorescent substance to 250 degrees C was shown in drawing 6 . Drawing 6 and drawing 4 show that the Maine glow peak temperature of thermoluminescence changed with operations of Dy added as a coactivator to 90 degrees C from 130 degrees C. Big luminescence from the trapping level equivalent to this temperature of 90 degrees C is SrAl 2O4. : As compared with Eu fluorescent substance, it is considered the cause which shows high brightness

at the time of those early stages of afterglow.
[0023] Sample 2-(2) - (7) SrAl 2O4 of a compounding ratio expressed in Table 3 to which the concentration of a dysprosium was changed by the approach as the above-mentioned that next it is the same : Eu and Dy fluorescent substance sample (sample 2-(2) - (7)) were adjusted.
[0024]
[Table 3]

試料	原料配合比			
	炭酸ストロンチウム	アルミナ	ユウロピウム	ジスプロシウム
試料2-(2)	0.99499 モル	1.0 モル	0.005 モル	0.00001モル
(3)	0.9895	1.0	0.005	0.00005
(4)	0.985	1.0	0.005	0.0025
(5)	0.94	1.0	0.005	0.025
(6)	0.92	1.0	0.005	0.035
(7)	0.79	1.0	0.005	0.10

[0025] This sample 2-(2) - (7) It is the result of having investigated the decay characteristic 2-(1) With the result of having investigated the decay characteristic, it was shown in Table 4. From this table 4, when the addition of Dy as a coactivator is based on excelling including after [10 minutes] brightness farther than ZnS:Cu phosphorescent materials, it is understood that 0.0025-0.05 mols are the optimal. Since it comes to have larger brightness than ZnS:Cu phosphorescent materials when 30 minutes or more pass after a stimulus halt even if it is the case where the addition of Dy is merely 0.00001 mols, the addition effectiveness of Eu and Dy which were used as an activator and a coactivator is clear. Moreover, since Dy is expensive, when the fall of economical efficiency and the decay characteristic by concentration quenching is taken into consideration, there will be no semantics in carrying out Dy more than 0.1 mol (ten-mol %) not much.
[0026] In addition, SrAl 2O4 : From it being an oxide system, Eu and Dy fluorescent substance are chemically stable compared with the conventional sulfide system phosphorescent materials, and excellent in lightfastness (Table 24 and 25 reference).
[0027]
[Table 4]

試料	10 分後輝度	30 分後輝度	100分後輝度
ZnS:Cu Std.	1. 00	1. 00	1. 00
試料2-(1)	12. 5	19. 6	37. 0
(2)	0. 943	1. 57	2. 00
(3)	1. 5	1. 7	2. 1
(4)	11. 7	17. 3	22. 1
(5)	20. 4	28. 6	40. 2
(6)	18. 6	26. 3	36. 4
(7)	1. 95	2. 66	3. 30

[0028] Next, the phosphorescent materials at the time of using neodium as a coactivator further are explained as an example 3, using a europium as an activator, using strontium as a metallic element (M).
Example 3.SrAl 2O4 : Composition and property sample 3-(1) of Eu and Nd fluorescent substance SrAl 2O4 of the compounding ratio shown in Table 5 to which the concentration of neodium was changed by the same approach as - (7) above-mentioned : Eu and Nd system

fluorescent substance sample (sample 3-(1) - (7)) were adjusted.
[0029]
[Table 5]

試料	原料配合比			
	炭酸ストロンチウム	アルミナ	ユウロピウム	ネオジウム
試料3-(1)	0.99499 モル	1.0 モル	0.005 モル	0.00001モル
(2)	0.9899	1.0	0.005	0.00005
(3)	0.985	1.0	0.005	0.0025
(4)	0.980	1.0	0.005	0.005
(5)	0.94	1.0	0.005	0.025
(6)	0.92	1.0	0.005	0.035
(7)	0.79	1.0	0.005	0.10

[0030] These sample 3-(1) - (7) The result of having investigated the decay characteristic was shown in Table 6.
[0031]
[Table 6]

試料	10 分後輝度	30 分後輝度	100分後輝度
ZnS:Cu Std.	1. 00	1. 00	1. 00
試料3-(1)	0. 71	0. 91	1. 12
(2)	0. 73	1. 02	1. 25
(3)	6. 20	8. 50	11. 14
(4)	9. 05	11. 75	14. 29
(5)	9. 01	11. 55	13. 98
(6)	8. 50	10. 21	11. 96
(7)	2. 35	2. 64	2. 86

[0032] This table 6 shows excelling ZnS:Cu phosphorescent materials in the decay characteristic including the brightness of 10 minutes after as it is the range whose addition of Nd as a coactivator is 0.0025-0.10 mols. Since it comes to have larger brightness than ZnS:Cu phosphorescent materials when about 60 minutes pass after a stimulus halt even if it is the case where the addition of Nd is merely 0.00001 mols, the addition effectiveness of Eu and Nd which were used as an activator and a coactivator is clear. Moreover, since Nd is expensive, when the fall of economical efficiency and the decay characteristic by concentration quenching is taken into consideration, there will be no semantics in carrying out Nd more than 0.1 mol (ten-mol %) not much.
[0033] In addition, SrAl 2O4 : From it being an oxide system, Eu and Nd fluorescent substance are chemically stable compared with the conventional sulfide system phosphorescent materials, and excellent in lightfastness (Table 24 and 25 reference). SrAl 2O4 furthermore according to this invention : the thermoluminescence property (glow curve) from the room temperature at the time of carrying out the luminous stimulus of Eu and the Nd fluorescent substance to 250 degrees C -- sample 3- (4) ******** -- the investigated result was shown in drawing 7 . It turns out that the Maine glow peak temperature of the thermoluminescence of the fluorescent substance which added Nd as a coactivator from drawing is about 50 degrees C.
[0034] Next, the phosphorescent materials at the time of using either of the elements of a lanthanum, a cerium, a praseodymium, samarium, a gadolinium, a terbium, a holmium, an erbium, a thulium, an ytterbium, a lutetium, manganese, tin, and a bismuth are further explained as an

example 4 as a coactivator, using a europium as an activator, using strontium as a metallic element (M).
[0035] Moreover, about an activator and each coactivator, from the example at the time of using europium and neodium, or a dysprosium, when about 0.005 mols add respectively to a metallic element (M), it takes that high afterglow brightness is obtained into consideration here, and it is Eu concentration 0.5 of an activator. Mol% (0.005 mols) and concentration 0.5 of a coactivator It illustrated only about the sample of mol % (0.005 mols).
Example 4.SrAl 2O4 : The result of having investigated the decay characteristic about the fluorescent substance sample which added a lanthanum, a cerium, a praseodymium, samarium, a gadolinium, a terbium, a holmium, an erbium, a thulium, an ytterbium, a lutetium, manganese, tin, and a bismuth as a coactivator by the approach of effectiveness previous statement of the coactivator of others in Eu system fluorescent substance was shown in Table 7.
[0036] It compares with the decay characteristic of the commercial ZnS:Cu fluorescent substance used as a criterion so that clearly from this table 7, and is which SrAl 2O4. : Since the decay characteristic of Eu system fluorescent substance sample will improve if it goes through the long duration for after [a stimulus halt] 30 minutes thru/or, and 100 minutes or more, it turns out that it is in practical use level enough. In addition, SrAl 2O4 : From it being an oxide system, Eu system fluorescent substance is chemically stable compared with the conventional sulfide system phosphorescent materials, and excellent in lightfastness (Table 24 and 25 reference).
[0037]
[Table 7]

試料	10 分後輝度	30 分後輝度	100分後輝度
ZnS:Cu Std.	1. 00	1. 00	1. 00
$SrAl_2O_4$:Eu,La	0. 33	0. 74	1. 14
$SrAl_2O_4$:Eu,Ce	0. 46	0. 93	1. 35
$SrAl_2O_4$:Eu,Pr	1. 24	2. 63	7. 51
$SrAl_2O_4$:Eu,Sm	3. 40	4. 82	9. 0
$SrAl_2O_4$:Eu,Gd	0. 51	1. 30	2. 27
$SrAl_2O_4$:Eu,Tb	1. 46	2. 81	7. 54
$SrAl_2O_4$:Eu,Ho	1. 06	2. 09	6. 29
$SrAl_2O_4$:Eu,Er	0. 63	1. 43	3. 18
$SrAl_2O_4$:Eu,Tm	0. 81	1. 53	3. 28
$SrAl_2O_4$:Eu,Yb	0. 61	1. 28	2. 99
$SrAl_2O_4$:Eu,Lu	0. 49	1. 01	3. 40
$SrAl_2O_4$:Eu,Mn	0. 81	1. 86	5. 57
$SrAl_2O_4$:Eu,Sn	1. 93	3. 61	7. 92
$SrAl_2O_4$:Eu,Bi	0. 72	1. 77	5. 55

[0038] Next, although a europium is used as an activator, using calcium as a metallic element (M) Calcium is used as the phosphorescent materials when not using a coactivator, and a metallic element. A europium is used as an activator. As a coactivator A lanthanum, a cerium, The case where at least one element of a group which consists of a praseodymium, neodium, samarium, a gadolinium, a terbium, a dysprosium, a holmium, an erbium, a thulium, an ytterbium, a lutetium, manganese, tin, and bismuths is used is explained as an example 5.
Example 5.CaAl 2O4 : Only what added the europium to composition and the calcium carbonate of a property special grade chemical of Eu system phosphorescent materials, and the alumina as

europium oxide (Eu 2O3) as an activator, To this, as a coactivator A lanthanum, a cerium, a praseodymium, neodium, As opposed to what added either of the elements of samarium, a gadolinium, a terbium, a dysprosium, a holmium, an erbium, a thulium, an ytterbium, a lutetium, manganese, tin, and a bismuth with the oxide, respectively Furthermore, it is boric acid as flux. After carrying out 5g (0.08 mols) addition and fully mixing using a ball mill, 1300 degrees C of this sample were calcinated for 1 hour using the electric furnace in the nitrogen-hydrogen mixed-gas (97:3) air current (flow rate: 0.1l. per minute). It is what cooled over about 1 hour to the room temperature after that, classified the obtained compound fine particles with the screen, and passed 100 meshes Fluorescent substance sample 5-(1) It considered as - (42).
[0039] In addition, sample 5-(2) obtained here The result of XRD analysis was shown in drawing 8 . Drawing to this fluorescent substance is CaAl 2O4 of monoclinic system. Consisting of a crystal became clear. next, sample 5- which used neodium, samarium, a dysprosium, and thorium for the coactivator as an example of representation -- (10) and 5- (16) and 5- the result of having investigated the thermoluminescence property (glow curve) was shown in drawing 9 and drawing 1010 about (22) and 5-(28). Since all have a glow peak in a pyrosphere 50 degrees C or more, it is suggested that these fluorescent substances have the long decay characteristic. When the emission spectrum of the afterglow was furthermore measured about the sample, as drawing 11 showed, any fluorescent substance of the emission peak wavelength was about 442nm blue luminescence.
[0040] Then, the result of having conducted comparison investigation of each decay characteristic relatively by making into a criterion CaSrS:Bi (trade-name BA-S: luminescence wavelength of 454nm by Nemoto& Co., Ltd.) of the phosphorescent materials of blue luminescence marketed from the former was shown in Table 8 thru/or 13. From Table 8 to CaAl 2O4 : Even if sensitization was carried out greatly and it used which coactivator by adding a coactivator about Eu fluorescent substance as there were some from which near brightness is obtained almost on a par with a commercial reference standard after 100 minutes and it was further shown in Table 9 thru/or 13 although the brightness at the time of the early stages of afterglow was low when Eu was 0.005 mols (0.5-mol %), the fluorescent substance with high enough practicality was able to be obtained [.]. It is in ** that the phosphorescent materials of blue luminescence of super-high brightness with it are obtained, and it can be called an epoch-making fluorescent substance. [about Nd, Sm, and especially Tm] [the very large addition effectiveness and] [brighter single or more figures than a commercial item] The result of having investigated the decay characteristic covering the long time of the high brightness fluorescent substance obtained by coactivating this Nd, Sm, and Tm to drawing 12 was shown.
[0041] In addition, it is 5-(1) as phosphorescent materials when not using a coactivator, although a europium is used for a detail as an activator, using calcium as a metallic element (M). - (6) The decay characteristic of the shown phosphorescent materials was shown in Table 8.
[0042]
[Table 8]

試料	10 分後輝度	30 分後輝度	100分後輝度
Std. CaSrS:Bi	1. 00	1. 00	1. 00
5-(1) $CaAl_2O_4$:Eu (Eu: 0.001モル%)	0. 18	0. 16	0. 14
(2) $CaAl_2O_4$:Eu (Eu: 0.01モル%)	0. 21	0. 18	0. 17
(3) $CaAl_2O_4$:Eu (Eu: 0.1 モル%)	0. 25	0. 27	0. 35
(4) $CaAl_2O_4$:Eu (Eu: 0.5 モル%)	0. 41	0. 60	0. 90
(5) $CaAl_2O_4$:Eu (Eu: 2.5 モル%)	0. 37	0. 45	0. 65
(3) $CaAl_2O_4$:Eu (Eu:10 モル%)	0. 25	0. 28	0. 39

[0043] Moreover, it is 5-(7) as phosphorescent materials at the time of using neodium as a coactivator, using a europium as an activator, using calcium as a metallic element (M). The decay characteristic of the phosphorescent materials shown in - (12) was shown in Table 9.
[0044]
[Table 9]

試 料	10 分後輝度	30 分後輝度	100分後輝度
Std. CaSrS:Bi	1.00	1.00	1.00
(7) $CaAl_2O_4$:Eu,Nd (Eu:0.5 mol% Nd:0.001 mol%)	0.53	0.76	1.01
(8) $CaAl_2O_4$:Eu,Nd (Eu:0.5 mol% Nd:0.01 mol%)	1.05	1.83	2.60
(9) $CaAl_2O_4$:Eu,Nd (Eu:0.5 mol% Nd:0.1 mol%)	8.68	11.8	20.3
(10) $CaAl_2O_4$:Eu,Nd (Eu:0.5 mol% Nd:0.5 mol%)	9.87	14.0	25.0
(11) $CaAl_2O_4$:Eu,Nd (Eu:0.5 mol% Nd:2.5 mol%)	3.18	4.61	8.05
(12) $CaAl_2O_4$:Eu,Nd (Eu:0.5 mol% Nd:10 mol%)	0.84	1.18	2.02

[0045] Furthermore, the decay characteristic of the phosphorescent materials shown in 5-(13) - (18) was shown in Table 10 as phosphorescent materials at the time of using samarium as a coactivator, using a europium as an activator, using calcium as a metallic element (M).
[0046]
[Table 10]

試 料	10 分後輝度	30 分後輝度	100分後輝度
Std. CaSrS:Bi	1.00	1.00	1.00
(13) $CaAl_2O_4$:Eu,Sm (Eu:0.5 mol% Sm:0.001 mol%)	0.71	0.98	1.23
(14) $CaAl_2O_4$:Eu,Sm (Eu:0.5 mol% Sm:0.01 mol%)	0.94	1.43	2.56
(15) $CaAl_2O_4$:Eu,Sm (Eu:0.5 mol% Sm:0.1 mol%)	4.21	6.32	11.30
(16) $CaAl_2O_4$:Eu,Sm (Eu:0.5 mol% Sm:0.5 mol%)	4.61	7.00	12.5
(17) $CaAl_2O_4$:Eu,Sm (Eu:0.5 mol% Sm:2.5 mol%)	2.14	3.26	5.80
(18) $CaAl_2O_4$:Eu,Sm (Eu:0.5 mol% Sm:10 mol%)	0.63	0.96	1.71

[0047] Moreover, the decay characteristic of the phosphorescent materials shown in 5-(19) - (24) was shown in Table 11 as phosphorescent materials at the time of using a dysprosium as a coactivator, using a europium as an activator, using calcium as a metallic element (M).
[0048]
[Table 11]

試 料	10 分後輝度	30 分後輝度	100分後輝度
Std. CaSrS:Bi	1.00	1.00	1.00
(19) $CaAl_2O_4$:Eu,Dy (Eu:0.5 mol% Dy:0.001 mol%)	0.30	0.24	0.20
(20) $CaAl_2O_4$:Eu,Dy (Eu:0.5 mol% Dy:0.01 mol%)	0.41	0.39	0.36
(21) $CaAl_2O_4$:Eu,Dy (Eu:0.5 mol% Dy:0.1 mol%)	0.52	0.60	0.76
(22) $CaAl_2O_4$:Eu,Dy (Eu:0.5 mol% Dy:0.5 mol%)	0.76	0.90	1.25
(23) $CaAl_2O_4$:Eu,Dy (Eu:0.5 mol% Dy:2.5 mol%)	0.84	1.18	1.78
(24) $CaAl_2O_4$:Eu,Dy (Eu:0.5 mol% Dy:10 mol%)	0.60	0.68	0.78

[0049] Moreover, the decay characteristic of the phosphorescent materials shown in 5-(25) - (30) was shown in Table 12 as phosphorescent materials at the time of using a thulium as a coactivator, using a europium as an activator, using calcium as a metallic element (M).
[0050]
[Table 12]

試 料	10 分後輝度	30 分後輝度	100分後輝度
Std. CaSrS:Bi	1.0	1.0	1.0
(25) $CaAl_2O_4$:Eu,Tm (Eu:0.5 mol% Tm:0.001 mol%)	1.04	1.36	1.81
(26) $CaAl_2O_4$:Eu,Tm (Eu:0.5 mol% Tm:0.01 mol%)	2.09	2.68	3.75
(27) $CaAl_2O_4$:Eu,Tm (Eu:0.5 mol% Tm:0.1 mol%)	4.89	6.78	8.70
(28) $CaAl_2O_4$:Eu,Tm (Eu:0.5 mol% Tm:0.5 mol%)	6.55	9.04	16.6
(29) $CaAl_2O_4$:Eu,Tm (Eu:0.5 mol% Tm:2.5 mol%)	0.634	1.19	2.68
(30) $CaAl_2O_4$:Eu,Tm (Eu:0.5 mol% Tm:10 mol%)	0.161	0.368	0.755

[0051] In addition, the decay characteristic of the phosphorescent materials shown in 5-(31) - (42) was summarized as phosphorescent materials at the time of using either of the elements of a lanthanum, a cerium, a praseodymium, a gadolinium, a terbium, a holmium, an erbium, an ytterbium, a lutetium, manganese, tin, and a bismuth as a coactivator, using a europium as an activator, using calcium as a metallic element (M), and it was shown in Table 13.
[0052] In addition, at the phosphorescent materials shown in this 5-(31) - (42), both the europium and other coactivators as an activator are 0.5. It adds mol % every.
[0053]
[Table 13]

試 料	10 分後輝度	30 分後輝度	100分後輝度
Std. CaSrS:Bi	1.00	1.00	1.00
(31) $CaAl_2O_4$:Eu,La (Eu:0.5 mol% La:0.5 mol%)	0.52	0.87	0.81
(32) $CaAl_2O_4$:Eu,Ce (Eu:0.5 mol% Ce:0.5 mol%)	0.84	1.23	1.96
(33) $CaAl_2O_4$:Eu,Pr (Eu:0.5 mol% Pr:0.5 mol%)	0.58	0.82	1.13
(34) $CaAl_2O_4$:Eu,Gd (Eu:0.5 mol% Gd:0.5 mol%)	0.66	0.91	1.26
(35) $CaAl_2O_4$:Eu,Tb (Eu:0.5 mol% Tb:0.5 mol%)	0.84	1.31	2.08
(36) $CaAl_2O_4$:Eu,Ho (Eu:0.5 mol% Ho:0.5 mol%)	0.88	1.33	2 39
(37) $CaAl_2O_4$:Eu,Er (Eu:0.5 mol% Er:0.5 mol%)	0.56	0.76	0.96
(38) $CaAl_2O_4$:Eu,Yb (Eu:0.5 mol% Yb:0.5 mol%)	0.70	0.91	1.28
(39) $CaAl_2O_4$:Eu,Lu (Eu:0.5 mol% Lu:0.5 mol%)	0.68	0.90	1.24
(40) $CaAl_2O_4$:Eu,Mn (Eu:0.5 mol% Mn:0.5 mol%)	0.31	0.42	0.58
(41) $CaAl_2O_4$:Eu,Sn (Eu:0.5 mol% Sn:0.5 mol%)	0.45	0.58	0.73
(42) $CaAl_2O_4$:Eu,Bi (Eu:0.5 mol% Bi:0.5 mol%)	0.25	0.23	0.48

[0054] Next, although neodium is used as a coactivator, using a europium as an activator, using calcium as a metallic element (M), the case where other coactivators are added is explained to coincidence as an example 6.
Example 6.CaAl 2O4 : A europium is added to composition and the calcium carbonate of a property special grade chemical of Eu and Nd system phosphorescent materials, and an alumina as europium oxide (Eu 2O3) as an activator. As the thing which added neodium to this as a coactivator, and a coactivator of further others Lanthanums other than neodium, a cerium, a praseodymium, samarium, Either of the elements of a gadolinium, a terbium, a dysprosium, a holmium, an erbium, a thulium, an ytterbium, a lutetium, manganese, tin, and a bismuth to what was added with the oxide, respectively It is boric acid as flux. After carrying out 5g (0.08 mols) addition and fully mixing using a ball mill, 1300 degrees C of this sample were calcinated for 1 hour using the electric furnace in the nitrogen-hydrogen mixed-gas (97:3) air current (flow rate: 0.1l. per minute). It is what cooled over about 1 hour to the room temperature after that, classified the obtained compound fine particles with the screen, and passed 100 meshes Fluorescent substance sample 6-(1) It considered as - (43).
[0055] here -- first -- Eu:0.5 Mol% and Nd:0.5 Mol% and other coactivator:0.5 as mol% -- various fluorescent substance samples -- adjusting -- after [10 minutes] brightness, after [30 minutes] brightness, and 100 a part -- back -- brightness -- it measured. It is the result 6-(1) As - (15), it is shown in Table 14.
[0056]
[Table 14]

試 料	10 分後輝度	30 分後輝度	100分後輝度
Std. CaSrS:Bi	1.0	1.0	1.0
$CaAl_2O_4$:Eu,Nd	9.87	14.0	25.0
6- (1) $CaAl_2O_4$:Eu,Nd,La	20.6	23.2	29.5
(2) $CaAl_2O_4$:Eu,Nd,Ce	12.7	17.5	26.9
(3) $CaAl_2O_4$:Eu,Nd,Pr	13.3	19.1	27.7
(4) $CaAl_2O_4$:Eu,Nd,Sm	8.20	12.6	22.6
(5) $CaAl_2O_4$:Eu,Nd,Gd	16.7	21.3	33.5
(6) $CaAl_2O_4$:Eu,Nd,Tb	13.8	17.2	25.6
(7) $CaAl_2O_4$:Eu,Nd,Dy	14.8	18.9	30.8
(8) $CaAl_2O_4$:Eu,Nd,Ho	16.5	21.6	34.3
(9) $CaAl_2O_4$:Eu,Nd,Er	15.9	21.0	33.8
(10) $CaAl_2O_4$:Eu,Nd,Tm	4.17	6.69	13.4
(11) $CaAl_2O_4$:Eu,Nd,Yb	11.0	16.9	27.9
(12) $CaAl_2O_4$:Eu,Nd,Lu	10.2	15.2	25.2
(13) $CaAl_2O_4$:Eu,Nd,Mn	6.45	8.01	11.9
(14) $CaAl_2O_4$:Eu,Nd,Sn	11.4	14.1	21.2
(15) $CaAl_2O_4$:Eu,Nd,Bi	10.5	13.5	21.4

[0057] As that in which especially afterglow brightness is excellent from this measurement result in the coactivator added with neodium, it was checked that they are a lanthanum, a dysprosium, a gadolinium, a holmium, an erbium, etc. It is there, next is Eu:0.5. Mol% and Nd:0.5 It is the concentration of a lanthanum after considering as mol% 0.1 It experimented by changing to ten-mol% from mol%. The result is shown in Table 15 as 6-(16) - (21).
[0058]
[Table 15]

試 料	10 分後輝度	30 分後輝度	100分後輝度
Std. CaSrS:Bi	1.0	1.0	1.0
(16) $CaAl_2O_4$:Eu,Nd Eu:0.5 mol% Nd:0.5 mol%	9.87	14.0	25.0
(17) $CaAl_2O_4$:Eu,Nd,La Eu:0.5 mol% Nd:0.5 mol% La:0.1 mol%	14.1	18.2	29.3
(18) $CaAl_2O_4$:Eu,Nd,La Eu:0.5 mol% Nd:0.5 mol% La:0.3 mol%	16.5	18.9	28.5
(1) $CaAl_2O_4$:Eu,Nd,La Eu:0.5 mol% Nd:0.5 mol% La:0.5 mol%	20.6	23.2	29.5
(19) $CaAl_2O_4$:Eu,Nd,La Eu:0.5 mol% Nd:0.5 mol% La:1.0 mol%	1.42	1.05	0.858
(20) $CaAl_2O_4$:Eu,Nd,La Eu:0.5 mol% Nd:0.5 mol% La:2.0 mol%	測定限界		
(21) $CaAl_2O_4$:Eu,Nd,La Eu:0.5 mol% Nd:0.5 mol% La:10 mol%	測定限界		

[0059] Eu: 0.5 Mol% and Nd:0.5 It is the concentration of a dysprosium after considering as mol% 0.1 It experimented by changing to ten-mol% from mol%. The result is shown in Table 16 as 6-(22) - (27).
[0060]

[Table 16]

区　　別	10 分後輝度	30 分後輝度	100分後輝度
Std. CaSr1:Bi	1. 0	1. 0	1. 0
[22] CaAl2O4:Eu,Nd Eu:0.5mol% Nd:0.5mol%	9. 67	14. 0	25. 0
[23] CaAl2O4:Eu,Nd,Dy Eu:0.5mol% Nd:0.5mol% Dy:0.1mol%	4. 32	6. 76	12. 0
[24] CaAl2O4:Eu,Nd,Dy Eu:0.5mol% Nd:0.5mol% Dy:0.2mol%	8. 91	14. 0	24. 2
[7] CaAl2O4:Eu,Nd,Dy Eu:0.5mol% Nd:0.5mol% Dy:0.5mol%	14. 8	18. 9	30. 8
[25] CaAl2O4:Eu,Nd,Dy Eu:0.5mol% Nd:0.5mol% Dy:1.0mol%	12. 1	18. 3	27. 8
[26] CaAl2O4:Eu,Nd,Dy Eu:0.5mol% Nd:0.5mol% Dy:2.0mol%	7. 49	10. 3	16. 0
[27] CaAl2O4:Eu,Nd,Dy Eu:0.5mol% Nd:0.5mol% Dy:10 mol%	1. 54	1. 29	0. 998

[0061] Eu: 0.5 Mol% and Nd:0.5 It is the concentration of a gadolinium after considering as mol% 0.1 It experimented by changing to ten-mol% from mol%. The result is shown in Table 17 as 6-(28) - (32).

[0062]

[Table 17]

区　　別	10 分後輝度	30 分後輝度	100分後輝度
Std. CaSr5:Bi	1. 0	1. 0	1. 0
CaAl2O4:Eu,Nd Eu:0.5mol% Nd:0.5mol%	9. 87	14. 0	25. 0
[28] CaAl2O4:Eu,Nd,Gd Eu:0.5mol% Nd:0.5mol% Gd:0.1mol%	11. 8	17. 4	30. 0
[29] CaAl2O4:Eu,Nd,Gd Eu:0.5mol% Nd:0.5mol% Gd:0.2mol%	12. 7	17. 8	29. 8
[5] CaAl2O4:Eu,Nd,Gd Eu:0.5mol% Nd:2.5mol% Gd:0.5mol%	16. 7	21. 3	33. 5
[30] CaAl2O4:Eu,Nd,Gd Eu:0.5mol% Nd:3.5mol% Gd:1.0mol%	10. 8	15. 7	28. 5
[31] CaAl2O4:Eu,Nd,Gd Eu:0.5mol% Nd:3.5mol% Gd:2.0mol%	16. 0	21. 7	29. 5
[32] CaAl2O4:Eu,Nd,Gd Eu:0.5mol% Nd:3.5mol% Gd :10 mol%	1. 01	0. 764	0. 590

[0063] Eu: 0.5 Mol% and Nd:0.5 After considering as mol%, it experimented by changing the concentration of a holmium to ten-mol% from 0.1-mol %. The result is shown in Table 18 as 6-(33) - (37).

[0064]

[Table 18]

区　　別	10 分後輝度	30 分後輝度	100分後輝度
Std. CaSr5:Bi	1. 0	1. 0	1. 0
CaAl2O4:Eu,Nd Eu:0.5mol% Nd:0.5mol%	9. 87	14. 0	25. 0
[33] CaAl2O4:Eu,Nd,Ho Eu:0.5mol% Nd:0.5mol% Ho:0.1mol%	10. 4	14. 4	25. 3
[34] CaAl2O4:Eu,Nd,Ho Eu:0.5mol% Nd:2.5mol% Ho:0.2mol%	12. 0	18. 2	27. 0
[8] CaAl2O4:Eu,Nd,Ho Eu:0.5mol% Nd:0.5mol% Ho:0.5mol%	16. 5	21. 6	34. 3
[35] CaAl2O4:Eu,Nd,Ho Eu:0.5mol% Nd:0.5mol% Ho:1.0mol%	13. 4	16. 9	26. 3
[36] CaAl2O4:Eu,Nd,Ho Eu:0.5mol% Nd:0.5mol% Ho:2.0mol%	13. 3	16. 0	23. 5
[37] CaAl2O4:Eu,Nd,Ho Eu:0.5mol% Nd:0.5mol% Ho:10 mol%	1. 20	0. 914	0. 782

[0065] Eu: 0.5 Mol% and Nd:0.5 After considering as mol%, it is from 0.1-mol % about the concentration of an erbium. It experimented by changing to five-mol%. The result is shown in Table 19 as 6-(38) - (43).

[0066]

[Table 19]

区　　別	10 分後輝度	30 分後輝度	100分後輝度
Std. CaSr5:Bi	1. 0	1. 0	1. 0
CaAl2O4:Eu,Nd Eu:0.5mol% Nd:0.5mol%	9. 87	14. 0	25. 0
[38] CaAl2O4:Eu,Nd,Er Eu:0.5mol% Nd:0.5mol% Er:0.1mol%	10. 7	15. 1	27. 0
[39] CaAl2O4:Eu,Nd,Er Eu:0.5mol% Nd:0.5mol% Er:0.2mol%	10. 3	14. 0	24. 0
[9] CaAl2O4:Eu,Nd,Er Eu:0.5mol% Nd:0.5mol% Er:0.5mol%	15. 9	21. 0	33. 8
[40] CaAl2O4:Eu,Nd,Er Eu:0.5mol% Nd:0.5mol% Er:1.0mol%	15. 4	21. 1	32. 3
[41] CaAl2O4:Eu,Nd,Er Eu:0.5mol% Nd:3.5mol% Er:2.0mol%	17. 3	21. 7	30. 8
[42] CaAl2O4:Eu,Nd,Er Eu:0.5mol% Nd:3.5mol% Er:3.0mol%	20. 1	21. 3	28. 5
[43] CaAl2O4:Eu,Nd,Er Eu:0.5mol% Nd:0.5mol% Er:5.0mol%	17. 5	17. 8	22. 0

[0067] From such a measurement result, mixing of two or more sorts of coactivators checked that there were some whose afterglow brightness improves. Furthermore, it is Eu:0.5 in that case. Mol% and Nd:0.5 Other coactivators are 0.5 after considering as mol%. It was also checked that the case where mol % extent addition is carried out shows the most excellent decay characteristic. Next, the phosphorescent materials at the time of using neodium or samarium as a coactivator further are explained as an example 7, using a europium as an activator, using barium as a metallic element (M).

example 7.BaAl 2O4 : Eu system fluorescent substance -- here -- Eu -- 0.5 a mol -- after doing % addition of -- further -- Nd or Sm -- 0.5 mol % of each -- what was added -- 7- (1) (2) ****** -- it is shown.

[0068] Moreover, although neodium was used for drawing 13 as a coactivator among these fluorescent substances, the emission spectrum of the afterglow after an excitation spectrum and

30 minutes after a stimulus halt pass was shown. Furthermore, although samarium was used as a coactivator, the emission spectrum of the afterglow after an excitation spectrum and 30 minutes after a stimulus halt pass was shown in drawing 14 .

[0069] Since each peak wavelength of an emission spectrum was green luminescence in about 500nm, it showed the afterglow reinforcement of after [a stimulus halt] 10 minutes, 30 minutes, and 100 minutes after in Table 20 by the relative value as compared with the ZnS:Cu phosphorescent materials (Nemoto [& Co., Ltd.] make: a name of article GSS, emission-peak-wavelength:530nm) which emit light green with a commercial item in the decay characteristic.

[0070]

[Table 20]

区　　別	10 分後輝度	30 分後輝度	100分後輝度
Std. ZnS:Cu	1. 0	1. 0	1. 0
BaAl2O4:Eu,Nd Eu:0.5mol% Nd:0.5mol%	1. 23	1. 14	0. 885
BaAl2O4:Eu,Sm Eu:0.5mol% Sm:0.5mol%	0. 982	0. 911	0. 768

[0071] From this table 20 to BaAl 2O4 : It turns out that Eu and Nd excel ZnS:Cu phosphorescent materials in afterglow brightness about 30 minutes after a stimulus halt. Moreover, BaAl 2O4 : The result to which afterglow brightness is inferior to ZnS:Cu phosphorescent materials in Eu and Sm a little was obtained. However, Eu or other coactivators are not added but it is BaAl 2O4. Since it is checked that fluorescence and afterglow are not accepted at all as a result of experimenting only as a crystal, it is clear that the activation effectiveness by Eu and Nd, or Sm addition is acquired.

[0072] In addition, BaAl 2O4 : From it being an oxide system, Eu system fluorescent substance is chemically stable compared with the conventional sulfide system phosphorescent materials, and excellent in lightfastness (Table 24 and 25 reference). Next, as a metallic element (M), the case where the mixture of calcium and strontium is used is explained as an example 8.

Example 8.SrX calcium1-X aluminum 2O4, respectively change a ratio, prepare composition and the strontium carbonate of a property special grade chemical of system phosphorescent materials, and a calcium carbonate, and an alumina is added to the sample. Furthermore, as an activator a europium as a coactivator A lanthanum, a cerium, To what added one element of a praseodymium, neodium, samarium, a gadolinium, a terbium, a dysprosium, a holmium, an erbium, a thulium, an ytterbium, a lutetium, manganese, tin, and a bismuth as flux -- for example, boric acid 5g (0.08 mol) addition -- carrying out -- the approach as stated above -- coming out -- SrX calcium1-X aluminum 2O4 The system fluorescent substance sample was compounded.

[0073] It is Sr0.5 calcium0.5 aluminum 2O4 as a representation property of the obtained fluorescent substance. : The result of having investigated the emission spectrum of the afterglow of Eu and Dy fluorescent substance (Eu0.5 mol %, Dy0.5 mol % addition) was shown in drawing 15 . If a part of Sr is permuted by calcium from drawing, the emission spectrum will be shifted to a short wavelength side, and it is SrAl 2O4. Luminescence and CaAl 2O4 by the system fluorescent substance That the afterglow of the neutral colors of luminescence of a system fluorescent substance can be obtained became whether to be **.

[0074] next -- as an activator and a coactivator -- Eu and Dy -- respectively -- 0.5-mol % -- added Srx calcium1-x aluminum 2O4 The result of having investigated the decay characteristic of a system fluorescent substance sample was shown in drawing 1618 . This drawing 16 shows that the high phosphorescent materials of the practicality which has the decay characteristic which excelled more than equivalent also about which fluorescent substance as compared with the commercial reference standard shown with the broken line in drawing are obtained.

[0075] Next, as a metallic element (M), the case where the mixture of strontium and barium is used is explained as an example 9.

Example 9.SrX Ba1-X aluminum 2O4, respectively change a ratio, prepare composition and the strontium carbonate of a property special grade chemical of system phosphorescent materials,

and a barium carbonate, and an alumina is added to the sample. Furthermore, as an activator a europium as a coactivator A lanthanum, a cerium, To what added one element of a praseodymium, neodium, samarium, a gadolinium, a terbium, a dysprosium, a holmium, an erbium, a thulium, an ytterbium, a lutetium, manganese, tin, and a bismuth It is boric acid as flux. 5g (0.08 mol) addition is carried out, and it is SrX Ba1-X aluminum 2O4 by the approach as stated above. The system fluorescent substance sample was compounded.

[0076] as the representation property of the obtained fluorescent substance -- Eu -- 0.5-mol % and Dy -- 0.5-mol % -- SrX Ba1-X aluminum 2O4 added and adjusted The result of having investigated the decay characteristic of a system fluorescent substance sample was shown in drawing 17 . This drawing 17 shows that the high phosphorescent materials of the practicality which has the decay characteristic which excelled more than equivalent also about which fluorescent substance as compared with the commercial reference standard shown with the broken line in drawing are obtained.

[0077] Next, as a metallic element (M), the case where the mixture of strontium and magnesium is used is explained as an example 10.

Example 10.SrX Mg1-X aluminum 2O4, respectively change a ratio, prepare composition and the strontium carbonate of a property special grade chemical of system phosphorescent materials, and a magnesium carbonate, and an alumina is added to the sample. Furthermore, as an activator a europium as a coactivator A lanthanum, a cerium, To what added one element of a praseodymium, neodium, samarium, a gadolinium, a terbium, a dysprosium, a holmium, an erbium, a thulium, an ytterbium, a lutetium, manganese, tin, and a bismuth It is boric acid as flux. 5g (0.08 mol) addition is carried out, and it is SrX Mg1-X aluminum 2O4 by the approach as stated above. The system fluorescent substance sample was compounded. as the representation property of the obtained fluorescent substance -- Eu -- 0.5-mol % and Dy -- 0.5-mol % -- SrXMg1-X aluminum 2O4 added and adjusted The result of having investigated the decay characteristic of a system fluorescent substance sample was shown in drawing 18 .

[0078] This drawing 18 shows that the high phosphorescent materials of the practicality which has the decay characteristic which excelled more than equivalent also about which fluorescent substance as compared with the commercial reference standard shown with the broken line in drawing are obtained except for the case where strontium/magnesium is 0.1/0.9. Next, as a metallic element (M), the case where two kinds of coactivators are used further is explained as an example 11, using a europium as an activator, using two or more metallic elements.

Example 11.calcium1-X SrX aluminum 2O4 : respectively change a ratio, prepare composition and the strontium carbonate of a property special grade chemical of Eu, Nd, and X fluorescent substance, and a calcium carbonate, and an alumina is added to the sample. further -- as an activator -- europium 0.5 mol % -- as a coactivator -- neodium 0.5 mol % -- adding -- as the coactivator of further others -- either of the elements of a lanthanum, a dysprosium, and a holmium -- 0.5-mol % -- to what was added as flux -- for example, boric acid 5g (0.08 mol) addition -- carrying out -- the approach as stated above -- coming out -- calcium1-X SrX aluminum 2O4 : Eu, Nd, and X system fluorescent substance sample 11- (1) - (9) It compounded and the decay characteristic was investigated.

[0079] first, the strontium carbonate and calcium carbonate of a special grade chemical -- respectively -- a ratio -- changing -- preparing -- the sample -- an alumina -- adding -- further -- as an activator -- europium 0.5 mol % -- as a coactivator -- neodium 0.5 mol % -- adding -- as the coactivator of further others -- a lanthanum -- 0.5-mol % -- what was added -- 11- (1) - (3) ** -- it carries out and is shown in Table 21.

[0080]

[Table 21]

試料	10分後輝度	30分後輝度	100分後輝度
Std. CaSrS:Bi	1.0	1.0	1.0
CaAl2O4:Eu,Nd	9.87	14.0	25.0
11-(1) (Ca0.8Sr0.2)Al2O4:Eu,Nd,La	18.2	17.1	19.0
(2) (Ca0.8Sr0.2)Al2O4:Eu,Nd,La	5.53	4.86	3.35
(3) (Ca0.8Sr0.2)Al2O4:Eu,Nd,La	6.30	3.08	測定限界

[0081] moreover, the strontium carbonate and calcium carbonate of a special grade chemical — respectively — a ratio — changing — preparing — the sample — an alumina — adding — further — as an activator — europium 0.5 mol % — as a coactivator — neodium 0.5 mol % — adding — as the coactivator of further others — a dysprosium — 0.5-mol % — what was added — 11- (4) - (8) ** — it carries out and is shown in Table 22.

[0082]

[Table 22]

試料	10分後輝度	30分後輝度	100分後輝度
Std. CaSrS:Bi	1.0	1.0	1.0
CaAl2O4:Eu,Nd	9.87	14.0	25.3
(4) (Ca0.8Sr0.2)Al2O4:Eu,Nd,Dy	13.2	14.8	20.4
(5) (Ca0.8Sr0.2)Al2O4:Eu,Nd,Dy	8.00	7.46	9.05
(6) (Ca0.8Sr0.2)Al2O4:Eu,Nd,Dy	3.36	3.08	測定限界

[0083] moreover, the strontium carbonate and calcium carbonate of a special grade chemical — respectively — a ratio — changing — preparing — the sample — an alumina — adding — further — as an activator — europium 0.5 mol % — as a coactivator — neodium 0.5 mol % — adding — as the coactivator of further others — a holmium — 0.5-mol % — what was added — 11- (7) - (9) ** — it carries out and is shown in Table 23.

[0084]

[Table 23]

試料	10分後輝度	30分後輝度	100分後輝度
Std. CaSrS:Bi	1.0	1.0	1.0
CaAl2O4:Eu,Nd	9.87	14.0	25.0
(7) (Ca0.8Sr0.2)Al2O4:Eu,Nd,Ho	13.9	15.3	21.4
(8) (Ca0.8Sr0.2)Al2O4:Eu,Nd,Ho	8.25	7.81	9.95
(9) (Ca0.8Sr0.2)Al2O4:Eu,Nd,Ho	2.91	2.62	3.65

[0085] Even if it was the case where added the europium as an activator and a metallic element (M) added two or more coactivators from these measurement results using two or more metallic elements (M) which consist of calcium and strontium, it has checked excelling compared with CaSrS:Bi including after [10 minutes] brightness.

The result of having investigated the resistance to humidity of the phosphorescent materials obtained by example 12. resistance-to-humidity trial this invention was shown in Table 24.

[0088] the constant temperature which carried out gas conditioning of two or more fluorescent substance samples to RH 40 degrees C and 95% in this investigation — it was left in the constant humidity chamber for 500 hours, and the brightness change before and behind that was measured. To humidity, neither of the fluorescent substances of the presentations is almost influenced, but a table shows that they is stable.

[0087]

[Table 24]

試料	試験前	試験後
SrAl2O4 : Eu,Dy (Eu:0.5mol% Dy:0.5mol%)	1.0	1.01
CaAl2O4 : Eu,Nd (Eu:0.5mol% Nd:0.5mol%)	1.0	0.99
Sr0.4Ca0.6Al2O4:Eu,Dy (Eu:0.5mol% Dy:0.5mol%)	1.0	1.00
Sr0.4Ba0.6Al2O4:Eu,Dy (Eu:0.5mol% Dy:0.5mol%)	1.0	0.99
Sr0.4Mg0.6Al2O4:Eu,Dy (Eu:0.5mol% Dy:0.5mol%)	1.0	1.02

[0088] The result of having performed the radiationproofing test of the phosphorescent materials obtained by example 13. lightfastness test-result this invention was shown in Table 25 as compared with the result of a zinc sulfide system fluorescent substance. This trial was put in according to JIS in the transparence container which carried out gas conditioning of the sample to saturated humidity, and measured Mitsuteru putting and a subsequent brightness change under the mercury-vapor lamp of 300W in the location of 30cm for 3 hours, 6 hours, and 12 hours.

[0089] A table shows that it is very stable as compared with the conventional zinc sulfide system fluorescent substance.

[0090]

[Table 25]

試料	試験前	3時間後	6時間後	12時間後
Std. ZnS:Cu	1.0	0.91	0.82	0.52
SrAl2O4 : Eu,Dy (Eu:0.5mol% Dy:0.5mol%)	1.0	1.01	1.00	1.01
CaAl2O4 : Eu,Nd (Eu:0.5mol% Nd:0.5mol%)	1.0	1.00	1.01	1.00
Sr0.4Ca0.6Al2O4:Eu,Dy (Eu:0.5mol% Dy:0.5mol%)	1.0	1.00	0.99	1.00
Sr0.4Ba0.6Al2O4:Eu,Dy (Eu:0.5mol% Dy:0.5mol%)	1.0	1.01	1.01	1.01
Sr0.4Mg0.6Al2O4:Eu,Dy (Eu:0.5mol% Dy:0.5mol%)	1.0	1.00	1.00	0.99

[0091] Although the phosphorescent materials by such this invention can also be used being able to apply to the front face of various products, they can also be used being able to mix in plastics, rubber, or glass. Furthermore, if it uses for the application of the dial face of ** replaced with the sulfide system phosphorescent materials currently used from the former, for example, various instruments, and a night train clock, a safety panel, etc., it will become what was extremely excellent from the prolonged high brightness decay characteristic.

[0092] Moreover, in addition to having the extremely excellent high brightness length decay characteristic, this fluorescent substance is chemically stable from being an oxide system, and, in addition to the conventional application, can newly consider the following applications from the point of excelling in lightfastness.

The display of a vehicle : An airplane, a ship, an automobile, a bicycle, a key, or the display:road traffic indicator of a keyhole indicator, Annunciators, such as a lane display, a display in a guard rail, a buoy for fishings, and a mountain path, The annunciator from a gate to the door, the display of the display outdoors to a helmet : The display of a signboard, a building, etc., keyhole

display indoor display [of an automobile]: — switch stationery [of an electric appliance]: — a writing implement, noctilucence ink, a map, and an astronomical-tables toy;jigsaw puzzle — substitution [0093] of the isotope used for the special back light discharge tube for the ball (it uses for clock etc.) liquid crystal for use:sports

[Effect of the Invention] As explained above, even if it compares with a commercial sulfide system fluorescent substance the sulfide system fluorescent substance known from the former about a completely different new phosphorescent-materials ingredient, it has long duration and the decay characteristic of high brightness far, and this invention's is chemically stable from being an oxide system further, and it is excellent in lightfastness.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] SrAl 2O4 : It is the graph which showed the result of having analyzed the crystal structure of Eu fluorescent substance by XRD.
[Drawing 2] SrAl 2O4 : It is the graph which showed the emission spectrum after the excitation spectrum of Eu fluorescent substance and 30 minutes after a stimulus halt pass.
[Drawing 3] SrAl 2O4 : It is the graph which showed the result of having compared the decay characteristic of Eu fluorescent substance with the decay characteristic of a Zn:S fluorescent substance.
[Drawing 4] SrAl 2O4 : It is the graph which showed the thermoluminescence property of Eu fluorescent substance.
[Drawing 5] SrAl 2O4 : It is the graph which showed the result of having compared the decay characteristic of Eu and Dy fluorescent substance with the decay characteristic of a Zn:S fluorescent substance.
[Drawing 6] SrAl 2O4 : It is the graph which showed the thermoluminescence property of Eu and Dy fluorescent substance.
[Drawing 7] SrAl 2O4 : It is the graph which showed the thermoluminescence property of Eu and Nd fluorescent substance.
[Drawing 8] CaAl 2O4 : It is the graph which showed the result of having analyzed the crystal structure of Eu system fluorescent substance by XRD.
[Drawing 9] CaAl 2O4 : It is the graph which showed the thermoluminescence property of the fluorescent substance using neodium or samarium as a coactivator among Eu system fluorescent substances.
[Drawing 10] CaAl 2O4 : It is the graph which showed the thermoluminescence property of the fluorescent substance using a dysprosium or thorium as a coactivator among Eu system fluorescent substances.
[Drawing 11] CaAl 2O4 : It is the graph which showed the emission spectrum after 5 minutes after a stimulus halt of Eu system fluorescent substance pass.
[Drawing 12] CaAl 2O4 : Eu, Sm fluorescent substance, and CaAl 2O4 : It is the graph which showed the result of having compared the decay characteristic of Eu and Nd fluorescent substance with the decay characteristic of a Zn:S fluorescent substance.
[Drawing 13] BaAl 2O4 : It is the graph which showed the emission spectrum after the excitation spectrum of Eu and Nd fluorescent substance and 30 minutes after a stimulus halt pass.
[Drawing 14] BaAl 2O4 : It is the graph which showed the emission spectrum after the excitation spectrum of Eu and Sm fluorescent substance and 30 minutes after a stimulus halt pass.
[Drawing 15] Sr0.5 calcium0.5 aluminum 2O4 : It is the graph which showed the emission spectrum of Eu and Dy fluorescent substance.
[Drawing 16] Srx calcium1-x aluminum 2O4 : It is a graph [the decay characteristic of a Zn:S fluorescent substance and a CaSrS:Bi fluorescent substance / decay characteristic / of Eu and Dy fluorescent substance].
[Drawing 17] Srx Ba1-x aluminum 2O4 : It is a graph [the decay characteristic of a Zn:S fluorescent substance / decay characteristic / of Eu and Dy fluorescent substance].

[Drawing 18] Srx Mg1-x aluminum 2O4 : It is a graph [the decay characteristic of a Zn:S fluorescent substance / decay characteristic / of Eu and Dy fluorescent substance].

[Translation done.]